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Simulation of the Thermal Conductivity of a Nanofluid with Small Particles by Molecular Dynamics Methods

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Abstract—The thermal conductivity of nanoliquids has been simulated by molecular dynamics method. We consider nanofluids based on argon with aluminum and zinc particles with sizes of 1−4 nm. The volume concentration of nanoparticles is varied from 1 to 5%. The dependence of the thermal conductivity on the volume concentration of nanoparticles has been analyzed. It has been shown that the thermal conductivity of a nanofluid cannot be described by classical theories. In particular, it depends on the particle size and increases with it. However, it has been established that the thermal conductivity of nanofluids with small particles can even be lower than that of the carrier fluid. The behavior of the correlation functions responsible for the thermal conductivity has been studied systematically, and the reason for the increase in the thermal conductivity of nanofluid has been explained qualitatively.

INTRODUCTION

It is well known that the thermal conductivity of solids (in particular metals, their oxides, graphite, and its derivatives) is several orders of magnitude higher than the thermal conductivity of fluid heat-transfer materials (water, ethylene glycol, various freons, etc.). The idea of using disperse fluids as heat-transfer and cooling agents was put forth long ago; however, traditional disperse liquids could not be used for this purpose due to sedimentation of disperse particles and their abrasivity. Disperse liquids with nanoparticles, called *nanofluids,* are free of these drawbacks. Even the first experiments on measuring their thermal conductivity [1, 2] demonstrated brilliant results; the addition of even small (on the order of the fraction of percent) concentrations of metal nanoparticles substantially increased the thermal conductivity of the basis liquid. Therefore, nanofluids can successfully be used for cooling engines and aggregates (in particular, in electronic system, heat and power engineering, transportation of heat, etc.). In 2008, Routbort with his colleagues developed a project on application of nanofluids as cooling agents in industrial units (see also [3]).

Since nanofluid flows are involved in all applications, reliable information on the thermalphysical characteristics of nanofluids is required to control the relevant processes. These characteristics are obviously not standard and cannot be described by classical theories developed for fluids with coarse particles. As regards viscosity, such understanding has been reached (see, for example, [4−9] and the literature cited therein). It was shown (both experimentally and using molecular dynamics simulation) that the viscosity of nanofluids substantially exceeds the viscosity of coarse-dispersed liquids with the same volume concentration of nanoparticles. However, in contrast to the latter case, the viscosity depends on the particle size and material, the nanofluids with the smaller particles have the larger viscosity. The reasons for these peculiarities are generally clear, although universal formulas have not been obtained and can hardly be expected.

The situation with the thermal conductivity of nanofluids is more complicated despite a very large number of publications devoted to its measurement. It has been established that the thermal conductivity of nanofluids attains a certain limiting level upon an increase in the particle concentration [10, 11]. In addition, it also depends on the nanoparticle size and increases with it. Experimental results concerning the excess of the thermal conductivity over the corresponding value for the carrier fluid are rather contradictory. It is usually pointed out that this quantity depends on the concentration and is always higher than the value predicted by the Maxwell's theory

$$\lambda = \lambda_f \left[1 + \frac{3(1-\varpi)\varphi}{1+2\varpi - \varphi(1-\varpi)} \right], \qquad (1)$$

where $\varpi = \lambda_f/\lambda_p$, λ_f and λ_p are the thermal conductivities of the carrier fluid and the material of particles, and φ is their volume concentration. The thermal conductivity of nanofluids is known to increase with the particle size, but what is its value in nanofluids with very tiny particles?

This study is devoted to analyze this question. It is extremely difficult to answer it experimentally because the number density of particles rapidly increases upon a decrease in their size (for a given volume concentration, it is inversely proportional to the third power of the particle radius). This leads to their active interaction, accompanied by the formation of conglomerates. As a result, the average size of particles and the correctness of the interpretation of experimental data change substantially. To avoid agglomeration, surface-active substances (surfactants) are conventionally used. However, a surfactant substantially changes the thermalphysical properties of a nanofluid, the effect being the stronger the smaller the nanoparticle size. On the other hand, the molecular dynamics method, which is characterized by the same predictability as experiment, makes it possible to conduct the experiment in the purest form (in particular using monodisperse particles). That is why, here, we are using precisely this method.

There is one more reason for applying the molecular dynamics method. The thermal conductivity of a nanofluid is a certain integral property of this nonstandard two-phase system. The experimental investigation of this property does not reveal the mechanisms that determining the thermal conductivity of nanofluids; the information on its dependence on certain parameters (the volume concentration of particles, their size, etc.) is quite rough. A large number of phenomenological models of heat conduction of nanofluids have been constructed based on different model concepts concerning, e.g., the effect of Brownian movement of particles (see review [12]). All of these models are extremely ingenious, but are usually based only on indirect physical considerations concerning the transport mechanisms in nanofluids. On the other hand, the molecular dynamics method makes it possible to investigate and analyze these mechanisms explicitly, which provides a solid foundation for constructing adequate macroscopic models of heat conduction in nanofluids.

The molecular dynamics simulation taking into account the different contributions to the thermal conductivity of nanofluids separately was carried out earlier. In particular, the thermal conductivity of xenon-based nanofluids with addition of nanoclusters of platinum atoms was modeled in [13]. However, that publication had a number of methodical drawbacks; its authors admitted that the thermal conductivity of the nanofluid, which is a binary system, was calculated using the formula for one-component systems and the contribution of diffusion was disregarded. In this study, we consider model nanofluids with argon as the carrier fluid and with spherical aluminum and zinc nanoparticles. The nanoparticle size was varied in the range of 1−4 nm, and their volume concentration was varied in the range of 1−5%.

1. SIMULATION TECHNIQUE

In simulation, we employed the standard molecular dynamics method. We used the original SibMD package that was applied earlier for solving various problems in the theory of transport of nanofluids [14−16]. The simulation was carried out in a cubic cell with periodic boundary conditions. The interaction of atoms of the carrier medium was determined by the Lennard-Jones potential

$$\Phi_{LJ}(r) = 4\varepsilon \left[(\sigma/r)^{12} - (\sigma/r)^6 \right], \qquad (2)$$

where σ is the effective diameter of molecules of the medium, ε is the depth of the potential well, and $r = |\mathbf{r}_i - \mathbf{r}_j|$ is the distance between the centers of the ith and jth molecules.

The interaction of molecules of the carrier medium with a nanoparticle was determined by the RK potential as follows [17]:

$$\Psi(r) = \Psi_9(r) - \Psi_3(r),$$
$$\Psi_i = C_i \left\{ \left[\frac{1}{(r-R)^i} - \frac{1}{(r+R)^i} \right] \right.$$
$$\left. - \frac{a_i}{r} \left[\frac{1}{(r-R)^{i-1}} - \frac{1}{(r+R)^{i-1}} \right] \right\}, \qquad (3)$$

where $i = 9, 3$, $a_9 = 9/8$, $a_5 = 3/2$, $C_9 = (4\pi\varepsilon_{12}\sigma_{12}^{12})/45V_p$, $C_3 = (2\pi\varepsilon_{12}\sigma_{12}^6)/3V_p$, and $V_p^{-1} = \rho_p/m_p$. Here, ρ_p is the density of the nanoparticle material, m_p is the atomic mass of the substance of the nanoparticle, R is the nanoparticle radius, and σ_{ij} and ε_{ij} are the parameters of potential (2) of the interactions of a carried medium molecule with a nanoparticle atom.

As the interaction potential for nanoparticles, we are using the potential [18], which has the following form for monodisperse particles:

$$U(r, R) = U_7(r, R) - U_1(r, R), \qquad (4)$$

$$U_7(r, R) = \frac{\pi^2}{315} \frac{\tilde{\varepsilon}\tilde{\sigma}^{12}}{V_p^2}$$

$$\times \left\{ \frac{R^2}{r} \left[\frac{1}{(r-2R)^7} + \frac{2}{r^7} + \frac{1}{(r+2R)^7} \right] \right.$$
$$- \frac{R}{3r} \left[\frac{1}{(r-2R)^6} - \frac{1}{(r+2R)^6} \right]$$
$$\left. - \frac{1}{30r} \left[\frac{1}{(r-2R)^5} - \frac{2}{r^5} + \frac{1}{(r+2R)^5} \right] \right\},$$

$$U_1(r, R) = \frac{2\pi^2}{3} \frac{\tilde{\varepsilon}\tilde{\sigma}^6}{V_p^2} \left[\ln\left(\frac{r^2 - 4R^2}{r^2} \right) \right.$$
$$\left. + 2R^2 \left(\frac{1}{r^2 - 4R^2} + \frac{1}{r^2} \right) \right].$$

Here, R is the nanoparticle radius and $\tilde{\varepsilon}$ and $\tilde{\sigma}$ are the parameters of the Lennard–Jones potential (2) of the interactions between nanoparticle atoms. Potentials (3) and (4) are constructed under the assumption that the interaction of atoms (molecules) of the carrier medium with nanoparticle atoms and the interactions between nanoparticle atoms are described by potentials of type (1) with parameters σ_{12}, ε_{12} and $\tilde{\sigma}$, $\tilde{\varepsilon}$, respectively.

The simulation was performed as follows. Molecules of the medium and nanoparticle were distributed uniformly in the simulation cell in accordance with the preset values of the carrier medium density and the volume concentration of nanoparticles. The density of the carrier medium was defined by virial parameter $\rho = N\sigma^3/V$; the volume of the simulation cell for the nanofluid was defined by the relation $V = \alpha N_1\sigma^3/\sqrt{2} + 4\pi\beta N_2 R^3/3$, where N_1 and N_2 are the numbers of fluid and nanoparticle molecules, respectively, and $\alpha = V/V_0$, $V_0 = N\sigma^3/\sqrt{2}$ being the volume of densely packed N molecules. After the addition of nanoparticles, coefficient β was chosen such that the pressure of the nanofluid is equal to the pressure of the carrier fluid with a preset density.

The initial velocities of molecules were defined in accordance with the Maxwellian distribution at a given temperature, while the initial velocities of nanoparticles were assumed to be zero. Calculations began after the initial relaxation period, when the entire system achieved equilibrium. The Newton equations were integrated using the Verlet integration scheme.

Since the range of the potentials used here is equal to infinity, the potential must be truncated in the course of simulation. The cutoff radius for potential (2) was 2.5σ, while for potential (3), it was chosen so that the force exerted on an argon atom by a nanoparticle over the cutoff radius of potential (3) is equal to the force of interaction of two molecules over the cutoff radius for potential (2). The potential of nanoparticles was truncated at a distance at which the force of interaction of nanoparticles was zero; i.e., we used the so-called soft-sphere potential.

The parameters of the interaction potential for the argon molecules were as follows: $\sigma = 3.405$ Å and $\varepsilon/k_B = 119.8$ K [19]. To calculate the parameters of potentials (3) and (4), we used the following parameters of potential (2): $\alpha = 2.46$ Å and $\varepsilon/k_B = 1040$ K for zinc [20] and $\sigma = 2.551$ Å and $\varepsilon/k_B = 857.6$ K for aluminum. The latter parameters were obtained from the data on the Young modulus and the crystal lattice structure (face-centered cubic (fcc) lattice) using the

method analogous to that described in [21]. Parameters σ_{12} and ε_{12} were determined using the simplest combination relations $\sigma_{12} = \sqrt{\sigma\tilde{\sigma}}$ and $\varepsilon_{12} = \sqrt{\varepsilon\tilde{\varepsilon}}$.

Since the phase trajectories of the system are locally unstable and mixed in the molecular dynamic calculation [22, 23], the obtained results must be averaged over the ensemble of independent phase trajectories. In this study, averaging was carried out over 1000 independent phase trajectories.

The thermal conductivity of a nanofluid (binary mixture) was calculated based on the fluctuation–dissipation theorem, which connects the thermal conductivity with the correlation function of the corresponding dynamic variables (such relations are usually referred to as Green–Kubo formulas). The complexity of the calculation of the thermal conductivity of the binary mixture under investigation lies in the need to eliminate the diffusion heat flux. When this is done, the thermal conductivity of the nanofluid assumes the form [24]

$$\lambda = \lambda_0 - \lambda_d \equiv \frac{L_0}{T^2} - \frac{L_2^2}{L_{22}T^2}. \tag{5}$$

The coefficients that appear in this expression are equal to the integrals of equilibrium correlation functions

$$L_0 = \frac{V}{3} \int_0^\tau \langle \mathbf{j}_Q(0)\mathbf{j}_Q(t) \rangle dt,$$
$$L_{22} = \frac{V}{3} \int_0^\tau \langle \mathbf{j}_{d2}(0)\mathbf{j}_{d2}(t) \rangle dt, \tag{6}$$

$$L_2 = \frac{V}{6} \int_0^\tau \langle \mathbf{j}_Q(0)\mathbf{j}_{d2}(t) \rangle dt + \frac{V}{6} \int_0^\tau \langle \mathbf{j}_{d2}(0)\mathbf{j}_Q(t) \rangle dt. \tag{7}$$

Angle brackets in these expressions indicate averaging over the ensemble and τ is the time of achieving the plateau value [25]. The diffusion flux of nanoparticle (second component) $\mathbf{j}_{d2}$ and heat flux $\mathbf{j}_Q$ that appear in these formulas are defined by the relations

$$\mathbf{j}_{d2}(t) = \frac{1}{V} \sum_{\alpha=2, i=1}^{N_2} \mathbf{v}_{2,i}(t),$$
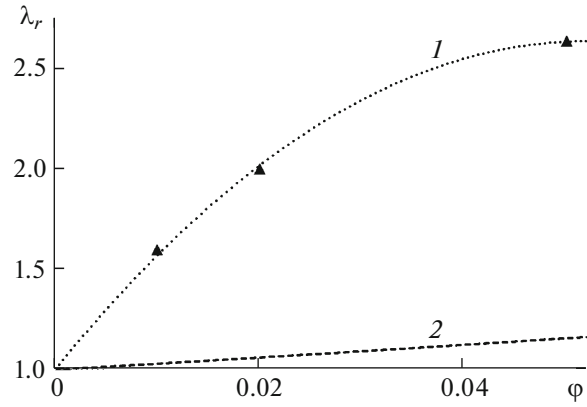$$\mathbf{j}_Q(t) = \mathbf{j}_Q^K(t) + \mathbf{j}_Q^P(t) + \mathbf{j}_Q^C(t). \tag{8}$$

The last expression contains three different terms, $\mathbf{j}_Q^K$, $\mathbf{j}_Q^P$, and $\mathbf{j}_Q^C$, which specify the heat flux associated with the transfer of the kinetic and potential energy, as well as the heat flux that appears as a result of the collisions, respectively. These contributions are defined as
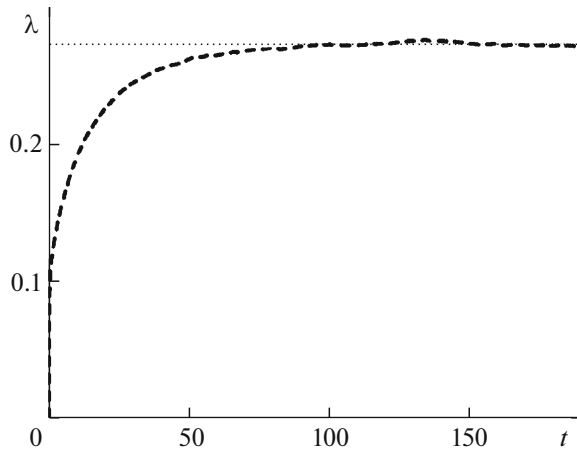
Fig. 1. Evolution of the thermal conductivity of Ar–Zn nanofluid, W/(mK), $d = 2$ nm, $\varphi = 4.2\%$.

Fig. 2. Dependence of the relative thermal conductivity of Ar–Zn nanofluid on the volume concentration of nanoparticles ($d = 2$ nm).

$$\mathbf{j}_Q^K(t) = \frac{1}{V}\left[\frac{m_1}{2}\sum_{\alpha=1, i=1}^{N_1}\mathbf{v}_{1,i}(t)v_{1,i}^2(t) + \frac{m_2}{2}\sum_{\alpha=2, i=1}^{N_2}\mathbf{v}_{2,i}(t)v_{2,i}^2(t)\right],$$

$$\mathbf{j}_Q^P(t) = \frac{1}{V}\left[\frac{1}{2}\sum_{\alpha=1, i=1}^{N_1}\sum_{\alpha=1, j\neq i}\mathbf{v}_{1,i}(t)\Phi_{11,ij}(r_{ij}(t))\right.$$

$$+ \frac{1}{2}\sum_{\alpha=1, i=1}^{N_1}\sum_{\alpha=2, j=i}^{N_2}\mathbf{v}_{1,i}(t)\Phi_{12,ij}(r_{ij}(t))$$

$$+ \frac{1}{2}\sum_{\alpha=2, i=1}^{N_2}\sum_{\alpha=1, j=i}^{N_1}\mathbf{v}_{2,i}(t)\Phi_{12,ij}(r_{ij}(t))$$

$$+ \left.\frac{1}{2}\sum_{\alpha=2, i=1}^{N_2}\sum_{\alpha=2, j\neq i}\mathbf{v}_{2,i}(t)\Phi_{22,ij}(r_{ij}(t))\right],$$

$$\mathbf{j}_Q^C(t) = \frac{1}{V}\left[\frac{1}{2}\sum_{\alpha=1, i=1}^{N_1}\sum_{\alpha=1, j\neq i}\mathbf{r}_{ij}(t)(\mathbf{F}_{11,ij}(t)\mathbf{v}_{1,i}(t))\right.$$

$$+ \frac{1}{2}\sum_{\alpha=1, i=1}^{N_1}\sum_{\alpha=2, j=i}^{N_2}\mathbf{r}_{ij}(t)(\mathbf{F}_{12,ij}(t)\mathbf{v}_{2,j}(t))$$

$$+ \frac{1}{2}\sum_{\alpha=2, i=1}^{N_2}\sum_{\alpha=1, j=i}^{N_1}\mathbf{r}_{ij}(t)(\mathbf{F}_{12,ij}(t)\mathbf{v}_{1,j}(t))$$

$$+ \left.\frac{1}{2}\sum_{\alpha=2, i=1}^{N_2}\sum_{\alpha=2, j\neq i}\mathbf{r}_{ij}(t)(\mathbf{F}_{22,ij}(t)\mathbf{v}_{2,j}(t))\right].$$

(9)

Here, index $\alpha = 1$ corresponds to argon atoms; $\alpha = 2$ corresponds to nanoparticles; m_i is the mass of a particle (atom or nanoparticle); V is the system volume; T is the temperature of the medium; $\Phi_{11, ij}$ are the poten-

tials of interaction of atoms in the carrier fluid; $\Phi_{12, ij}$ are the potentials of interaction of its atoms and particles; $\Phi_{22, ij}$ are the potentials of interaction of particles; $\mathbf{F}_{\alpha\beta, ij}$ are the corresponding forces; and N_1 and N_2 are the numbers of argon atoms and nanoparticles, respectively.

2. SIMULATION RESULTS

In accordance with relations (5)–(7), the thermal conductivity being simulated is a function of time. The value of the thermal conductivity is obtained when the integration time attains the plateau value of τ, at which it stops changing. The evolution of function $\lambda(t)$ (5) that defines the thermal conductivity is shown in Fig. 1 for a nanofluid with zinc particles of size 2 nm. The volume concentration of particles was 4.2% and the mass fraction was 0.208. The time in this case was measured in the units of $\tau_0 = \sigma/c$, where c is the thermal velocity of molecules of the carrier medium. The plateau value was attained over time intervals of about $100\tau_0$.

A typical dependence of relative thermal conductivity $\lambda_r = \lambda/\lambda_f$ of the same nanofluid as in Fig. 1 on the volume concentration of nanoparticles ($\rho = 0.707$, $T = 300$ K) is shown in Fig. 2. Here, triangles mark the results of simulation and dashed line 2 corresponds to formula (1). The thermal conductivity of the given nanofluid considerably exceeds the thermal conductivity of the carrier fluid as well as of coarse-disperse fluids (1). For example, the thermal conductivity of a 2% nanofluid is almost twice as high as the value given by formula (1).

The dependence of the thermal conductivity of a nanofluid for a low (up to 10–15%) concentration of nanoparticles is usually successfully described by a quadratic dependence on their volume concentration φ of the form
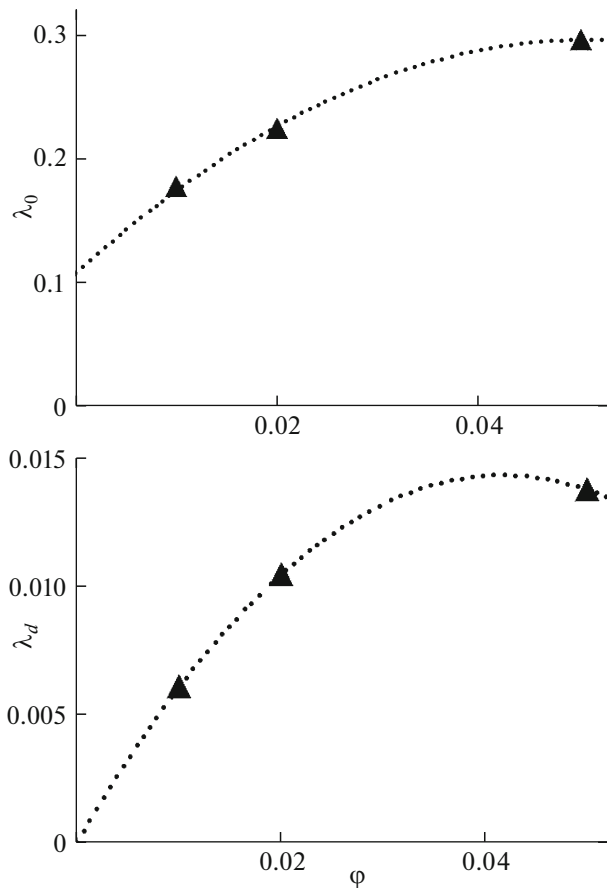
Fig. 3. Dependence of coefficients λ_0 and λ_d (W/mK) on volume concentration of nanoparticles ($d = 2$ nm).

Fig. 4. Dependences of the relative thermal conductivity of Ar–Zn and Ar–Al nanofluids on the nanoparticle diameter (nm).

$$\lambda_r = \lambda/\lambda_f = 1 + a_1\varphi - a_2\varphi^2. \qquad (10)$$

In Fig. 2, this expression corresponds to the dotted curve *1* (in this case, $a_1 = 63.1$ and $a_2 = 607.9$). The presence of the second term with the negative sign in formula (10) indicates that, upon an increase in the concentration, the thermal conductivity of the nanofluid achieves a certain limiting value. As mentioned above, this was also observed in the experiments. On the other hand, the thermal conductivity for low concentrations of nanoparticles (when the second term in formula (10) can be omitted) increases linearly with the concentration. In this case, the relative excess of thermal conductivity $\Delta = (\lambda_r - 1)$ is about 20 times larger than the value predicted by the Maxwell theory.

As follows from relation (5), the thermal conductivity of a nanofluid is a superposition of two terms. The first term λ_0 is present in both the expression for the pure fluid (one-component medium) and the nanofluid, while the second term λ_d only appear for the nanofluid. The dependence of these terms on the volume concentration of particles is shown in Fig. 3. Here, triangles correspond to the calculation results and dotted curves are their approximations of
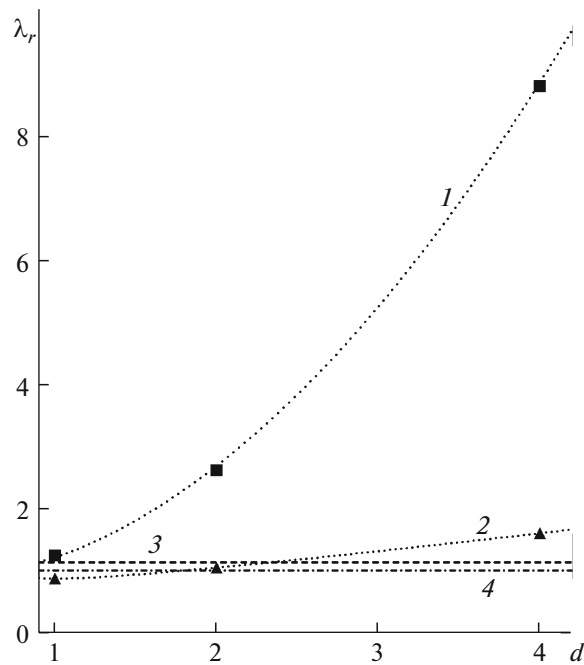
type (10). The contribution of the diffusion term is small and decreases beginning with a certain concentration. This is quite natural, since the diffusion of nanoparticles becomes weaker upon an increase in their concentration.

To determine the dependence of the thermal conductivity on the nanoparticle diameter, we considered two nanofluids based on argon with zinc and aluminum nanoparticles. In both cases, the volume concentration of nanoparticles was 4.2%, the density of the carrier fluid was $\rho = 0.707$, and the temperature was $T = 300$ K. The results are shown in Fig. 4. Here, the squares and curve *1* correspond to the nanofluid with zinc particles, curve *2* was obtained for the nanofluid with aluminum nanoparticles, line *3* is the value calculated by formula (1) for suspensions with the same volume concentration of nanoparticles, and line *4* describes the results for pure argon. The results obtained for these two nanofluids differ significantly. The thermal conductivity of the nanofluid with zinc particles is always substantially higher than the thermal conductivity of the carrier fluid and than the value determined by formula (1). Conversely, the thermal conductivity of the nanofluid with aluminum nanoparticles of size 1 nm is lower than that of the carrier fluid. However, the thermal conductivity of a nanofluid with particle of size 4 nm exceeds the value determined by formula (1).

In classical theories of the heat conduction of coarse-dispersed fluids, the material of disperse particles is taken into account in terms of their thermal

conductivity (see formula (1)). However, the situation in nanofluids with metal nanoparticles is different. These particles have a thermal conductivity that exceeds that of the carrier fluid by several orders of magnitude ($\lambda_f \ll \lambda_p$); in this case, formula (1) becomes independent of the particle material and assumes the simple form $\lambda_r = (1 + \varphi)/(1 - \varphi)$. Therefore, classical theories do not in fact yield the dependence of the thermal conductivity of disperse fluids on the particle material. Nevertheless, the results considered here show that this dependence exists. For example, the thermal conductivity of Ar–Zn nanofluid with zinc nanoparticles of diameter 2 nm and a volume concentration of 4.2% is approximately 2.4 times higher than the corresponding value for the Ar–Al nanofluid. However, the density of zinc is also higher than the density of aluminum. Therefore, we can state that the thermal conductivity of a nanofluid depends on the particle material (increases with its density).

3. ANALYSIS OF DIFFERENT CONTRIBUTIONS TO THERMAL CONDUCTIVITY

Analysis of expressions (6)–(9) shows that the thermal conductivity is determined by a number of various contributions (heat transfer as a result of motion of atoms of the fluid and nanoparticles, their interaction, etc.). To find the reason for the substantial excess of the thermal conductivity of a nanofluid over the corresponding value for the carrier fluid, we must analyze all possible components. The contribution λ_0 to thermal conductivity (5) is the sum of six components as follows:

$$\lambda_0 = \lambda_0^K + \lambda_0^P + \lambda_0^C + \lambda_0^{KP} + \lambda_0^{KC} + \lambda_0^{PC}, \quad (11)$$

$$\lambda_0^K = \frac{V}{3k_B T^2} \int_0^\tau \chi_0^K(t)dt = \frac{V}{3k_B T^2} \int_0^\tau \mathbf{j}_Q^K(0)\mathbf{j}_Q^K(t)dt,$$

$$\lambda_0^P = \frac{V}{3k_B T^2} \int_0^\tau \chi_0^P(t)dt = \frac{V}{3k_B T^2} \int_0^\tau \mathbf{j}_Q^P(0)\mathbf{j}_Q^P(t)dt,$$

$$\lambda_0^C = \frac{V}{3k_B T^2} \int_0^\tau \chi_0^C(t)dt = \frac{V}{3k_B T^2} \int_0^\tau \mathbf{j}_Q^C(0)\mathbf{j}_Q^C(t)dt,$$

$$\lambda_0^{KP} = \frac{2V}{3k_B T^2} \int_0^\tau \chi_0^{KP}(t)dt = \frac{2V}{3k_B T^2} \int_0^\tau \mathbf{j}_Q^K(0)\mathbf{j}_Q^P(t)dt,$$

$$\lambda_0^{KC} = \frac{2V}{3k_B T^2} \int_0^\tau \chi_0^{KC}(t)dt = \frac{2V}{3k_B T^2} \int_0^\tau \mathbf{j}_Q^K(0)\mathbf{j}_Q^C(t)dt,$$

$$\lambda_0^{PC} = \frac{2V}{3k_B T^2} \int_0^\tau \chi_0^{PC}(t)dt = \frac{2V}{3k_B T^2} \int_0^\tau \mathbf{j}_Q^P(0)\mathbf{j}_Q^C(t)dt.$$

Diffusion contribution λ_d to (5) can also be represented analogously as shown below:

$$\lambda_d = \lambda_d^K + \lambda_d^P + \lambda_d^C + \lambda_d^{KP} + \lambda_d^{KC} + \lambda_d^{PC}$$
$$= \frac{1}{T^2 L_{22}}[(L_2^K)^2 + (L_2^P)^2 + (L_2^C)^2 + 2L_2^K L_2^P \quad (12)$$
$$+ 2L_2^K L_2^C + 2L_2^P L_2^C],$$

$$L_2^K = \frac{V}{3}\int_0^T \langle \mathbf{j}_Q^K(0)\mathbf{j}_{d2}(t)\rangle dt, \quad L_2^P = \frac{V}{3}\int_0^T \langle \mathbf{j}_Q^P(0)\mathbf{j}_{d2}(t)\rangle dt,$$

$$L_2^C = \frac{V}{3}\int_0^T \langle \mathbf{j}_Q^C(0)\mathbf{j}_{d2}(t)\rangle dt.$$

As a result, we can calculate all six contributions to the thermal conductivity of a nanofluid: kinetic (superscript K), potential (P), collisional (C), kinetic–potential (KP), kinetic–collisional (KC), and potential–collisional (PC) as follows:

$$\lambda^K = \lambda_0^K - \lambda_d^K = \frac{1}{T^2}\left[L_0^K - \frac{(L_2^K)^2}{L_{22}}\right],$$

$$\lambda^P = \lambda_0^P - \lambda_d^P = \frac{1}{T^2}\left[L_0^P - \frac{(L_2^P)^2}{L_{22}}\right],$$

$$\lambda^C = \lambda_0^C - \lambda_d^C = \frac{1}{T^2}\left[L_0^C - \frac{(L_2^C)^2}{L_{22}}\right],$$

$$\lambda^{KP} = \lambda_0^{KP} - \lambda_d^{KP} = \frac{1}{T^2}\left[L_0^{KP} - 2\frac{L_2^K L_2^P}{L_{22}}\right], \quad (13)$$

$$\lambda^{KC} = \lambda_0^{KC} - \lambda_d^{KC} = \frac{1}{T^2}\left[L_0^{KC} - 2\frac{L_2^K L_2^C}{L_{22}}\right],$$

$$\lambda^{PC} = \lambda_0^{PC} - \lambda_d^{PC} = \frac{1}{T^2}\left[L_0^{PC} - 2\frac{L_2^C L_2^P}{L_{22}}\right].$$

The results of calculations for argon and argon-based nanofluids with zinc particles of diameters 2 and 4 nm for their volume concentration $\varphi = 4.2\%$ and mass concentration $C_2 = 0.208$ are given in Table 1. The pressure in nanofluids was equal to the pressure of pure Ar at density $\rho = 0.707$ and temperature $T = 300$ K. The main contribution to the thermal conductivity of pure argon comes from coefficients L^C (62%), which determine the energy flux associated with collisions between argon atoms, and L^{KC} (22%), which is associated with the correlation between the kinetic energy flux and the energy flux due to collisions. This is not surprising, since the density of argon is high. In this case, the kinetic heat transfer (L^K) associated with the motion of molecules is small and amounts to only 8%.

What is the difference between the thermal conductivity structure for a nanofluid and pure argon? It can be seen from the table that both positive and negative contributions appear for the studied binary sys-

tems. Physically, this means that, along with the conventional heat flux, a flux matched with the temperature gradient (negative thermal conductivity) also appears. As for a pure fluid, the collisional contribution λ^C is important; in nanofluids, it is 1.5 times larger for a nanofluid with a particle diameter of 2 nm and 3.6 times larger for a nanofluid with a particle diameter of 4 nm. However, the largest contribution to the thermal conductivity comes from the term λ^{KC}. It amounts to 50% of the total thermal conductivity for a nanofluid with 2-nm particles and to almost 80% for a nanofluid with 4-nm particles. Kinetic contribution λ^K is also significant (34% of the total value λ for a nanofluid with a nanoparticle diameter of 2 nm and 45% for a nanofluid with 4-nm particles). Therefore, the higher values of the thermal conductivity of a nanofluid compared to the pure fluid are mainly due to the considerable increase in the kinetic (λ^K) and kinetic–collisional (λ^{KC}) contributions.

4. EVOLUTION OF CORRELATION FUNCTIONS

To estimate different mechanisms of the elevation of the thermal conductivity in nanofluids, it is important to know not only the magnitude of different contributions, but also the dynamics of the corresponding correlation functions. The evolution of the correlation functions $\chi_0^K(t)$, $\chi_0^C(t)$, and $\chi_0^{KC}(t)$ of the heat flux (see formulas (11)), which make the largest contribution to the thermal conductivity, is illustrated in Fig. 5. The top panel corresponds to argon and the bottom panel for an argon-based nanofluid with zinc particles of diameter 2 nm ($\varphi = 4.2\%$). The correlation functions $\chi(t)$ are normalized to $\chi^K(0)$ for pure argon, while the time is normalized to τ_0. The correlation functions $\chi_0^K(t)$, $\chi_0^C(t)$, and $\chi_0^{KC}(t)$ correspond to curves *1*, *2*, and *3*, respectively. For pure argon, all correlation functions decay exponentially rapidly with a characteristic time on the order of the time of interaction between molecules. The evolution of the correlation functions for nanofluids is more complicated. It was shown in [26] that the autocorrelations velocity function (ACVF) for a nanoparticle is a superposition of two exponential functions. The relaxation time of the first exponential function is on the order of the time of interaction of a nanoparticle with individual molecules of the carrier fluid, while the relaxation time for the second function is on the order of the time of interaction of a nanoparticle with microscopic fluctuations of hydrodynamic fields of the carrier medium. The latter time is usually several times larger than the former time. The correlation functions that determine the main contributions to the thermal conductivity of the nanofluid behave analogously. Their evolution also occurs in two stages. At the first stage, the relaxation time is equal to the relaxation time of the cor-

Table 1. Contributions of different terms to thermal conductivity, W/m K

λ	Ar	Ar–Zn ($d = 2$ nm)	Ar–Zn ($d = 4$ nm)
λ_0		0.282163011	0.807266812
λ_d		0.0131916228	0.0117404684
λ	0.10680659	0.268971388	0.795526344
λ_0^K		0.13939356	0.555674513
λ_d^K		0.0478870749	0.199758098
λ^K	0.00853276	0.0915064848	0.355916415
λ_0^C		0.0965082435	0.235437078
λ_d^C		0.0023135801	0.000153929297
λ^C	0.06503381	0.0941946634	0.235283149
λ_0^P		0.0163644013	0.10063356
λ_d^P		0.0231271266	0.123198502
λ^P	0.00050646	−0.00676272531	−0.0225649413
λ_0^{KC}		0.156042641	0.63243097
λ_d^K		0.0210514212	0.0110902883
λ^K	0.02352531	0.13499122	0.621340682
λ_0^{KP}		−0.083342968	−0.464380266
λ_d^{KP}		−0.0665579581	−0.313750846
λ^{KP}	0.00262643	−0.02207763387	−0.15062942
λ_0^{KC}		−0.0388115389	−0.252529043
λ_0^{PC}		−0.014629622	−0.00870950256
λ^{PC}	0.00658181	−0.0241819169	−0.243819541

relation functions of the thermal conductivity of the carrier fluid, but beginning from a time instant of approximately $2\tau_0$, it is described by a certain relaxation time τ_f.

Let us consider the mechanisms of ACVF relaxation of a nanoparticle in greater detail. The kinetic mechanism is the more effective, the smaller the nanoparticle size and mass. Even for a particle of diameter 1−2 nm, its contribution to the total relaxation of correlation functions is small. Beginning from this size, the relaxation of correlation functions of a nanoparticle occurs predominantly due to its interaction with microfluctuations of the fields of the carrier fluid. It was shown in [27, 28] that the characteristic scale l_f of these fluctuations is on the order of the nanoparticle size (at least, for not very coarse particles). Therefore, relaxation time τ_f must be on the order of the time of the interactions of a disperse particle with a fluctuation, which in turn is determined by
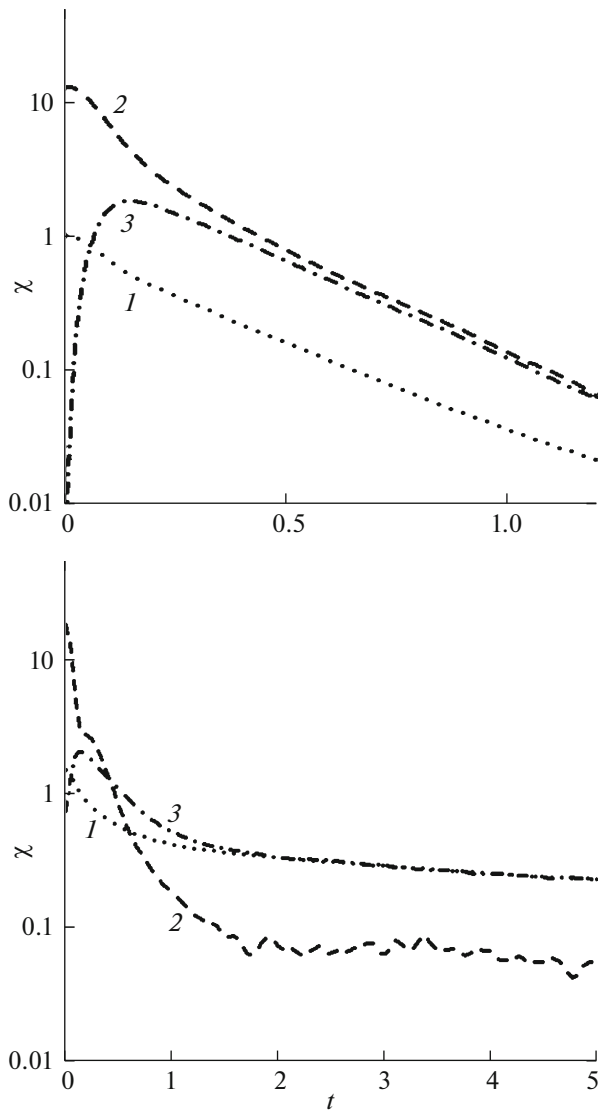
precisely this circumstance (see Fig. 5). A consequence of the slow relaxation of these correlation functions is considerably higher thermal conductivity of the nanofluid compared to the corresponding value for the carrier fluid. Estimate (14) also implies that relaxation time τ_f (and, hence, the thermal conductivity) increases with the size of nanoparticles and their density (mass).

CONCLUSIONS

First of all, the molecular dynamics simulation performed here leads to the conclusion that the thermal conductivity of nanofluids cannot be described by the Maxwell formula (1) (or its generalizations). The thermal conductivity of nanofluids with metal particles is independent of their thermal conductivity and can generally considerably exceed the value determined by formula (1). It increases with the particle concentration, but then attains a certain limiting value, after which it changes insignificantly. In contrast to all classical theories, the thermal conductivity of a nanofluid also depends on the nanoparticle size (increases with it). At the same time, in certain situations, the thermal conductivity of a nanofluid with a small particle size is not higher (or even lower) than the values predicted by the Maxwell theory. However, upon a further increase in the nanoparticle size, the thermal conductivity of the nanofluid gradually increases, then becomes higher than the values predicted by formula (1). Apart from the particle size, the effect of the elevated thermal conductivity is also determined by the density of the particle material. This effect (in particular, lower values of the thermal conductivity) depends on the ratio of the densities of the particle material and of the carrier fluid. This also follows from the results of molecular-dynamics simulation for a system of hard spheres [29]. In this connection with this, it is expedient to note that, with increasing density of the material of particles, their mass concentration in the nanofluid sharply increases. For example, in the argon-based nanofluids with aluminum particles considered here, for their fixed volume concentration equal to 4.2%, the mass fraction of aluminum particles was 0.09, while the corresponding value for zinc particles was 0.208. Therefore, the larger the mass fraction of particles, the higher the excess values of the thermal conductivity of the nanofluid over the corresponding value for the carrier fluid.

A generally accepted model of heat conduction of nanofluid has not been developed as yet despite the large number of attempts at constructing such a model (see review [12] and the literature cited therein). Moreover, the reason for the abnormal excess of the thermal conductivity of nanofluids over the values observed for conventional disperse liquids in fact remain unclear. Various possible reasons have been discussed by many authors. This was probably done most systematically by Keblinski et al. [30, 31] and in

Fig. 5. Correlation functions of the heat flux fluctuations in pure argon and in Ar−Zn nanofluid.

ratio $\tau_f \sim l_f/c_p \sim R/c_p$, where c_p is the mean thermal velocity of a nanoparticle. This time can easily be connected with the time of interaction of molecules as follows:

$$\tau_f \sim \frac{R}{c_p} \sim \frac{R}{c}\sqrt{\frac{M}{m}} \sim \frac{R}{\sigma}\sqrt{\frac{M}{m}}\tau_0, \qquad (14)$$

where m and M are the mass of a carrier fluid molecule and a nanoparticle, respectively.

For nanoparticles considered here, time (14) is at least an order of magnitude longer than the characteristic time τ_0 of relaxation of carrier fluid molecules. In particular, this means that the characteristic decay of all correlation functions that determine the thermal conductivity of a nanofluid is an order of magnitude larger than for the carrier fluid. Calculations confirm

the review by Kleinstreuer and Feng [32], where the contributions of four possible mechanisms were analyzed. These authors considered the effect of (i) ballistic phonon transport of heat; (ii) the formation of a fluid layer around nanoparticles, which has an elevated thermal conductivity; (iii) the Brownian movement of nanoparticles; and (iv) their clusterization. The ballistic phonon mechanism of the formation of additional increase in thermal conductivity was rightfully rejected by almost all authors. In our simulation, this mechanism was disregarded because we treat nanoparticles as solids in which no energy transfer occurs.

With regard to the clusterization of nanoparticles, in principle, it could lead to an increase in the thermal conductivity. However, the following circumstance should be borne in mind. If the clusterization takes place, the fluid acquires particles of a macroscopic size. However, in this case, the thermal conductivity must become independent of the nanoparticle size (as in classical theories) on the one hand, but on the other hand, these particles should rapidly sediment. Neither of these effects has been observed in well-staged experiments (we assume that the average size of nanoparticles in well-staged experiments remains unchanged at least during the measuring stage, and the particle size distribution does not change noticeably). These nanofluids are undoubtedly used in actual experiments. This also follows from molecular dynamics calculations for a system of hard spheres [29], in which clusterization is ruled out in principle, but nevertheless a noticeable excess in the thermal conductivity over the value predicted by the Maxwell theory is detected. The results of our calculations based on the potential for soft spheres in the description of the interactions of nanoparticles also confirm this conclusion.

The Brownian movement of nanoparticles was repeatedly discussed as a possible mechanism responsible for the higher thermal conductivity of nanofluids compared to pure fluids. As correctly noted in [30, 31], the direct influence of Brownian movement of nanoparticles on the thermal conductivity of a nanofluid is weak. However, a nanofluid is a binary system of particles, in which active mutual diffusion of the components takes place. In this case, the presence of fluxes formed that apparently determines the main mechanism of heat conduction in nanofluids. As a result of the diffusion of nanoparticles and molecules, the contribution to the thermal conductivity associated with the fluxes of transferred kinetic energy may increase by an order of magnitude and even more.

As mentioned above, a layer of molecules of the carrier fluid with parameters correlated with those for a nanoparticle is indeed formed around nanoparticles. The presence of these layers in an ordered fluid substantially changes the heat flux associated with the transfer of the kinetic and potential energies of mole-

cules moving together with a nanoparticle. In the table, this corresponds to terms λ^K, λ^P, and λ^{KP}. This transfer in the nanofluid can indeed increase by more than an order of magnitude and, in our calculations, can make a significant contribution to the thermal conductivity of the nanofluid (the contribution of λ^K amounts to 45%).

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